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APPLICATIONS OF PHOTOCURABLE
PRE-CERAMIC POLYMERS

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1 This application is a continuation-in-part of an
2 application filed June 3, 1999 under Serial No. 09/325,524.

3 BACKGROUND OF THE INVENTION

4 The field of the invention is specific applications of
5 photo curable pre-ceramic polymer chemistry to specific
6 applications and more particularly to specific applications
7 such as impregnation and/or coating of ceramic filters for
8 use in combustion engine exhaust systems.

9 U. S. Patent No. 4,806,612 teaches preceramic acetylenic
10 polysilanes which contain $--(CH_2)_wC\equiv CR'$ groups
11 attached to silicon where w is an integer from 0 to 3 and
12 where R' is hydrogen, an alkyl radical containing 1 to 6
13 carbon atoms, a phenyl radical, or an $--SiR''(3)$ radical
14 wherein R'' is an alkyl radical containing 1 to 4 carbon
15 atoms. The acetylenic polysilanes are prepared by reacting

1 chlorine-or bromine-containing polysilanes with either a
2 Grignard reagent of general formula $R'C.tbd.C(CH_2)_wMgX'$
3 where w is an integer from 0 to 3 and X' is chlorine,
4 bromine, or iodine or an organolithium compound of general
5 formula $R'C.tbd.C(CH_2)_wLi$ where w is an integer from 0
6 to 3. The acetylenic polysilanes can be converted to
7 ceramic materials by pyrolysis at elevated temperatures
8 under an inert atmosphere.

9 U. S. Patent No. 4,800,211 teaches 3-Hydroxybenzo[b]
10 thiophene-2-carboxamide derivatives which have been prepared
11 by: (1) treating a substituted 2-halobenzoate with a
12 thioacetamide; (2) treating a substituted thiosalicylate
13 with an appropriately substituted haloacetamide; and (3)
14 further synthetic modification of compounds prepared above.
15 These compounds have been found to be effective inhibitors
16 of both cyclooxygenase and lipoxygenase and thereby useful
17 in the treatment of pain, fever, inflammation, arthritic
18 conditions, asthma, allergic disorders, skin diseases,

1 cardiovascular disorders, psoriasis, inflammatory bowel
2 disease, glaucoma or other prostaglandins and/or leukotriene
3 mediated diseases.

4 U. S. Patent 4,588,832 teaches a novel and economical
5 route for the synthetic preparation of a 1-alkynyl
6 trihydrocarbyl silane compound. The method includes the
7 steps of reacting metallic sodium with a hydrocarbyl-
8 substituted acetylene or allene compound to form a
9 substituted sodium acetylide and reacting the acetylide with
10 a trihydrocarbyl monohalogenosilane in the reaction mixture
11 which is admixed with a polar organic solvent such as
12 dimethylformamide.

13 U. S. Patent No. 4,505,726 teaches an exhaust gas
14 cleaning device provided with a filter member which collects
15 carbon particulates in exhaust gases discharged from a
16 diesel engine and an electric heater for burning off the
17 particulates collected by the filter member. The filter
18 member is composed of a large number of intersecting porous

1 walls which define a large number of inlet gas passages and
2 outlet gas passages which are adjacent to each other. The
3 electric heater is composed of at least one film-shaped
4 heating resistor which is directly formed on the upstream
5 end surface of the filter member so as to be integral
6 therewith. When the amount of carbon particulates collected
7 by the filter member reaches a predetermined level, electric
8 current is supplied to the electric heater. The carbon
9 particulates adhered to the upstream end surface of the
10 filter member are ignited and burnt off. Then, the
11 combustion of carbon particulates spreads to the other
12 carbon particulates collected in the other portion of the
13 filter member.

14 U. S. Patent No. 5,843,304 teaches a materials
15 treatment system which includes filtration and treatment of
16 solid and liquid components of a material, such as a waste
17 material. A filter or substrate assembly is provided which
18 allows liquids to pass therethrough, while retaining solids.

1 The solids are then incinerated utilizing microwave energy,
2 and the liquids can be treated after passing through the
3 filter element, for example, utilizing a treatment liquid
4 such as an oxidant liquid. The filter assembly can also
5 include an exhaust filter assembly which removes solids or
6 particulate matter from exhaust gasses, with the retained
7 solids/particulates incinerated utilizing microwave energy.

8 U. S. Patent No. 5,074,112 teaches a filter assembly
9 for an internal combustion engine which includes, in
10 combination, a housing defining an exhaust gas passage
11 having an inlet end and an outlet end and a cavity
12 intermediate the inlet and outlet ends thereof and in serial
13 fluid communication therewith, the cavity defining an
14 electromagnetically resonant coaxial line waveguide, a
15 filter disposed within the cavity for removing particulate
16 products of combustion from exhaust gases passing through
17 the cavity, and a mechanism for producing axisymmetrically
18 distributed, standing electromagnetic waves within the

1 cavity whereby to couple electromagnetic energy in the waves
2 into lossy material in the cavity to produce heat for
3 incinerating the particulate products of combustion
4 accumulated on the filter.

5 U. S. Patent No. 4,934,141 teaches a device for
6 microwave elimination of particles contained in the exhaust
7 gases of diesel engines in which a microwave source and a
8 conductor of the electromagnetic field generated by the
9 source is joined with a resonator mounted on an element of
10 the pipe for the exhaust gases which contains an insert,
11 characterized by the fact that the insert consists of a
12 filter whose upstream and downstream ends are offset toward
13 the inside of the cavity defined by the resonator and
14 delimit two chambers in which conductors of the electro-
15 magnetic field come out, respectively.

16 U. S. Patent No. 4,825,651 teaches a device and method
17 for separating soot or other impurities from the exhaust
18 gases of an internal-combustion engine, particularly a

1 diesel internal-combustion engine, comprises a microwave
2 source that is coupled to the intermediate section of the
3 exhaust pipe that is constructed for the development
4 of an electromagnetic field, an effective burning of the
5 soot with a low flow resistance, the intermediate section
6 being developed as a cavity resonator and at its exhaust gas
7 inlet and exhaust gas outlet, is equipped with a metal grid,
8 and an insert made of a dielectric material in the cavity
9 resonator concentrates the exhaust gas flow in the area of
10 high energy density of the electromagnetic field.

11 U. S. Patent No. 4,477,771 teaches conductive
12 particulates in the form of soot which are collected from
13 diesel engine exhaust gases on a porous wall monolithic
14 ceramic filter in such a way that the soot is somewhat
15 uniformly distributed throughout the filter. The filter is
16 housed in a chamber having a property of a microwave
17 resonant cavity and the cavity is excited with microwave
18 energy. As the particulates are collected the cavity appears

1 to the microwaves to have an increasing dielectric constant
2 even though the matter being accumulated is conductive
3 rather than dielectric so that as collected on the porous
4 filter it has the property of an artificial dielectric. The
5 response of the cavity to the microwave energy is monitored
6 to sense the effect of the dielectric constant of the
7 material within the cavity to provide a measure of the soot
8 content in the filter.

9 U. S. Patent No. 5,902,514 teaches a material for
10 microwave band devices which are used by the general people
11 and in industrial electronic apparatuses. Particularly, a
12 magnetic ceramic composition for use in microwave devices, a
13 magnetic ceramics for use in microwave devices and a
14 preparation method therefore are disclosed, in which the
15 saturation magnetization can be easily controlled, and a low
16 ferri-magnetic resonance half line width and an acceptable
17 curie temperature are ensured. The magnetic ceramic
18 composition for microwave devices includes yttrium oxide

1 (Y(2) O(3)), iron oxide (Fe(2) O(3)), tin oxide (SnO(2)),
2 aluminum oxide (Al(2) O(3)) and a calcium supply source.
3 The magnetic ceramics for the microwave devices are
4 manufactured by carrying out a forming and a sintering after
5 mixing: yttrium oxide, iron oxide, tin oxide, aluminum oxide
6 and calcium carbonate (or calcium oxide) based on a formula
7 shown below. It has a saturation magnetization of 100-1,800
8 G at the normal temperature, a temperature coefficient for
9 the saturation magnetization of 0.2%/ deg. C., and a ferri-
10 magnetic resonance half line width of less than 60 Oe, Y(3-
11 x) Ca(x/2) Sn(x/2) Fe(5-y) Al(y) O(12) where $0.1 \leq x \leq 1$, and
12 $0.1 \leq y \leq 1.5$.

13 U. S. Patent No. 5,843,860 teaches a ceramic
14 composition for high-frequency dielectrics which includes
15 the main ingredients of ZrO(2), SnO(2) and TiO(2) and a
16 subsidiary ingredient of (Mn(NO(3))(2).4H(2) O). A
17 homogeneous ceramic composition can be prepared by a process
18 which comprises the steps of: adding ZrO(2), SnO(2) and

1 TiO(2) by the molar ratio to satisfy (ZrO(2))(1-x)
2 (SnO(2))(x) (TiO(2))(1+y) (wherein, 0.1M deg. C. or above;
3 and, adding 1% or less of Mn(NO(3))(2).4H(2) O by weight of
4 MnO to the mixture. The ceramic composition of the
5 invention has a high dielectric constant of 40 or more, a
6 quality factor of 7000 or more, and a temperature
7 coefficient of resonance frequency below 10. Accordingly,
8 it can be used for an integrated circuit at microwave as
9 well as at high frequency, or for dielectric resonators.

10 U. S. Patent No. 5,808,282 teaches a microwave
11 susceptor bed which is useful for sintering ceramics,
12 ceramic composites and metal powders. The microwave
13 susceptor bed contains granules of a major amount of a
14 microwave susceptor material, and a minor amount of a
15 refractory parting agent, either dispersed in the susceptor
16 material, or as a coating on the susceptor material.
17 Alumina is the preferred susceptor material. Carbon is the
18 most preferred parting agent. A sintering process uses the

1 bed to produce novel silicon nitride products.

2 U. S. Patent No. 5,446,270 teaches a composition which
3 includes susceptors having the capability of absorbing
4 microwave energy and a matrix. The susceptors includes a
5 particulate substrate substantially non-reflective of
6 microwave energy and a coating capable of absorbing
7 microwave energy. The matrix is substantially non-
8 reflective of microwave energy. Susceptors are typically
9 particles having a thin-film coating thereon. The matrix
10 typically includes polymeric or ceramic materials that are
11 stable at temperatures conventionally used in microwave
12 cooking. The composition allows reuse of the susceptors,
13 eliminates decline in heating rate, eliminates arcing,
14 allows the heating rate to be controlled, allows overheating
15 to be controlled, and allows formation of microwave heatable
16 composite materials having very low metal content.

17 U. S. Patent No. 5,365,042 teaches a heat treatment
18 installation for parts made of a composite material which

1 has a ceramic matrix and which includes a treatment
2 enclosure. The treatment enclosure is connected to a
3 microwave generator by a wave-guide and which includes a
4 press for hot pressing a part to be treated in the enclosure
5 and a gas source for introducing a protective gas into the
6 enclosure.

7 U. S. Patent No. 5,126,529 teaches a method for forming
8 a three-dimensional object by thermal spraying which
9 utilizes a plurality of masks positioned and removed over a
10 work surface in accordance with a predetermined sequence.
11 The masks correspond to cross sections normal to a
12 centerline through the work-piece. One set of masks defines
13 all cross sections through the work-piece. A second set of
14 masks contains at least one mask. The mask corresponds to
15 each mask of the first set. Masks from each set are
16 alternatively placed above a work surface and sprayed with
17 either a deposition material from which the work-piece will
18 be made or a complementary material. In this manner, layers

1 of material form a block of deposition material and
2 complementary material. The complementary material serves
3 as a support structure during forming and is removed.
4 Preferably, the complementary material has a lower melting
5 temperature than the deposition material and is removed by
6 heating the block. Alternatively, one could mask only for
7 the deposition material and remove complementary material
8 overlying the deposition material after each spraying of
9 complementary material.

10 U. S. Patent No. 4,199,387 teaches an air filter unit
11 of the pleated media, high efficiency type. The media pleat
12 edges are sealed to the supporting frame to prevent bypass
13 of air with a ceramic adhesive and fibrous ceramic mat which
14 allows the unit to be exposed to high temperatures (e.g., up
15 to 2000 deg. F.) without danger of seal breakdown. While in
16 the form of a slurry the adhesive is applied, for example,
17 with a trowel to the zig-zag pleated edges of the media
18 which, together with corrugated spacers, forms the filter

1 core. The latter is then surrounded on four sides by the
2 compressible mat of fibrous ceramic material and inserted in
3 a box-like support frame with the slurry filling the space
4 between the pleated edges of the media and the fibrous mat.
5 The filter core and surrounding mat are assembled with the
6 support frame while the slurry is still wet whereby, upon
7 hardening, the resulting layers of ceramic cement provide a
8 complete, heat-resistant seal while avoiding cracking in
9 normal handling due to the resilience of the compressed
10 fibrous mat which maintains an airtight seal between
11 hardened ceramic and support frame.

12 U. S. Patent No. 6,063,150 teaches a self-cleaning
13 particle filter for Diesel engines which includes a filter
14 housing, control circuitry, a removable filter sandwich and
15 independent power source. The removable filter sandwich
16 includes a number of sintered metal strips sewn and
17 positioned between two sheets of inorganic material to
18 provide a filter sandwich. Current is delivered to the

1 metal filter strips to efficiently burn off carbon, lube oil
2 and unburned fuel particulates which have been filtered from
3 exhaust gas. The filter sandwich is formed into a
4 cylindrical configuration and mounted onto a perforated
5 metal carrier tube for receiving and filtering exhaust gas.

6 U. S. Patent No. 6,101,793 teaches an exhaust gas
7 filter having a ceramic filter body is configured such that
8 a specific heat h (cal/g deg. C.) of ceramic powder
9 constituting the body, and a bulk specific gravity d
10 (g/cm^3) of the filter, satisfy the relation 0.12
11 ($\text{cal/cm}^3 \text{ deg. C.}$) $\leq h \cdot d \leq 0.19$ ($\text{cal/cm}^3 \text{ deg. C.}$). The
12 ceramic filter body includes a plurality of cells which
13 extend axially to open at opposite ends of the body. One of
14 the opposite axial ends of each of the cells is closed by a
15 filler in such a manner that the closed ends of the cells
16 and the open ends of the cells are arranged in an
17 alternating configuration. The filter traps particulates in
18 the exhaust gas, and the trapped particulates are removed by

1 regeneration combustion of the filter. The filter exhibits
2 excellent durability, thus preventing the formation of
3 cracks in the surface and interior of the filter. When the
4 filter is mounted on a diesel engine, the diesel engine
5 advantageously does not discharge black smoke.

6 U. S. Patent No. 5,756,412 teaches a dielectric ceramic
7 composition for microwave applications which consists
8 essentially of the compound having a formula $B'B(2)O(6)$,
9 wherein B' is at least one metal selected from the group of
10 Mg, Ca, Co, Mn, Ni and Zn, and wherein B" is one of Nb or Ta,
11 and additionally includes at least one compound selected
12 from the group of CuO, $V(2)O(5)$, $La(2)O(3)$, $Sb(2)O(5)$,
13 $WO(3)$, $MnCO(3)$, MgO, $SrCO(3)$, ZNO, and $Bi(2)O(3)$ as an
14 additive, wherein the amount of the additive is 0.05% to
15 2.0% by weight of the total weight of the composition.

16 The synthesis of polycarbosilane from the pyrolytic
17 condensation reaction of polydimethylsilane obtained from
18 the reaction of dichlorodimethylsilane with an alkali metal,

1 such as sodium. In the latter approach, polydimethylsilane
2 can be prepared by Würtz type coupling of dichlorodimethyl-
3 silane with sodium in toluene. The direct pyrolysis of
4 polydimethylsilane, a viscous thermoplastic resin, at high
5 temperature gives SiC in a ceramic yield of about 30%-40%.
6 By thermally cross-linking the polydimethylsilane into an
7 infusible rigid thermoset polymer, which is insoluble in any
8 common solvents, the subsequent pyrolysis yield is on the
9 order of 88%-93%. This thermolysis was accomplished by
10 refluxing the polydimethyl-silane to in excess of 350°C.

11 Numerous pre-ceramic polymers with improved yields of
12 the ceramic have been described in U. S. Patent No.
13 5,138,080, U. S. Patent No. 5,091,271, U. S. Patent No.
14 5,051,215 and U. S. Patent No. 5,707,471. The fundamental
15 chemistry contained in these embodiments is specific to the
16 process employed and mainly leaves the pre-ceramic polymer
17 in a thermoplastic state. These pre-ceramic polymers which
18 catalytic or photo-induced cross-linking do not satisfy the

1 high ceramic yield, purity and fluidity in combination with
2 low temperature crosslinking ability necessary for producing
3 large densified ceramic structures in a single step
4 continuous process.

5 U. S. Patent No. 5,138,080 teaches a novel polysila-
6 methylenosilane polymers which has polysilane-poly-
7 carbosilane skeleton which can be prepared in one-step
8 reaction from mixtures of chlorosilaalkanes and organochloro
9 silanes with alkali metals in one of appropriate solvents or
10 in combination of solvents thereof. Such polysilamethyleno
11 silane polymers are soluble and thermoplastic and can be
12 pyrolyzed to obtain improved yields of silicon carbide at
13 atmospheric pressure.

14 U. S. Patent No. 5,091,271 teaches a shaped silicon
15 carbide-based ceramic article which has a mechanical
16 strength which is produced at a high efficiency by a process
17 including the step of forming an organic silicone polymer,
18 for example, polycarbosilastyrene copolymer, into a

1 predetermined shape, for example, a filament or film; doping
2 the shaped polymer with a doping material consisting of at
3 least one type of halogen, for example, bromine or iodine,
4 in an amount of 0.01% to 150% based on the weight of the
5 shaped polymer, to render the shaped polymer infusible; and
6 pyrolyzing the infusible shaped polymer into a shaped SiC-
7 based ceramic article at a temperature of 800° C to 1400° C
8 in an inert gas atmosphere, optionally the halogen-doped
9 shaped polymer being treated with a basic material, for
10 example, ammonia, before the pyrolyzing step, to make the
11 filament uniformly infusible.

12 U. S. Patent No. 5,300,605 teaches poly(I-hydro-1-R-1-
13 silapent-3-ene) homopolymers and copolymers which contain
14 silane segments with reactive silicon-hydride bonds and
15 contain hydrocarbon segments with cis and trans carbon-
16 carbon double bonds.

17 U. S. Patent No. 5,171,810 teaches random or block
18 copolymers with (I-hydro-I-R-I-sila-cis-pent-3-ene), poly(I-

1 hydro-1-R-3,4 benzo-1-sila pent-3-ene) and disubstituted I-
2 silapent-3-ene repeating units of the general formula ##STRI##
3 where R is hydrogen, an alkyl radical containing from one to
4 four carbon atoms or phenyl, R. sup. 1 is hydrogen, an alkyl
5 radical containing from one to four carbon atoms, phenyl or a
6 halogen and R.sup.2 is hydrogen, or R. sup.1 and R. sup. 2 are
7 combined to form a phenyl ring, are prepared by the anionic
8 ring opening polymerization of silacyclopent-3-enes or 2-
9 silaindane with an organometallic base and cation coordinating
10 ligand catalyst system or a metathesis ring opening catalyst
11 system.

12 U. S. Patent No. 5,169,916 Poly(I -hydro- I -R- I -
13 sila-cis-pent-3-ene) and poly(I -hydro- I -R-3,4 benzo-1-
14 sila pent-3-ene) polymers which has repeating units of the
15 general formula polycarbosilane containing at least two
16 tbd.SiH groups per molecule via intimately contacting such
17 fusible polycarbosilane with an effective hardening amount
18 of the vapors of sulfur.

1 U. S. Patent No. 5,064,915 teaches insoluble poly-
2 carbosilanes, readily pyrolyzed into silicon carbide ceramic
3 materials such as SiC fibers, are produced by hardening a
4 fusible polycarbosilane containing at least two tbd. SiH
5 groups per molecule via intimately contacting such fusible
6 polycarbosilane with an effective hardening amount of the
7 vapors of sulfur.

8 U. S. Patent No. 5,049,529 teaches carbon nitride ceramic
9 materials which are produced by hardening a fusible
10 polycarbosilane containing at least two tbd.SiH groups per
11 molecule by intimately contacting such fusible polycarbosilane
12 with an effective hardening amount of the vapors of sulfur,
13 next, heat treating the infusible polycarbosilane which
14 results under an ammonia atmosphere to such extent as to
15 introduce nitrogen into the infusible polycarbosilane without
16 completely removing the carbon therefrom and then heat
17 treating the nitrogenated polycarbosilane in a vacuum or in an

1 inert atmosphere to such extent as to essentially completely
2 convert it into a ceramic silicon carbon nitride.

3 U. S. Patent No. 5,051,215 teaches a rapid method of
4 infusibilizing pre-ceramic polymers which includes treatment
5 of the polymers with gaseous nitrogen dioxide. The
6 infusibilized polymers may be pyrolyzed to temperatures in
7 excess of about 800°C to yield ceramic materials with low
8 oxygen content and, thus, good thermal stability. The methods
9 are especially useful for the production of ceramic fibers
10 and, more specifically, to the on-line production of ceramic
11 fibers.

12 U. S. Patent No. 5,028,571 teaches silicon nitride
13 ceramic materials which are produced by hardening a fusible
14 polycarbosilane containing at least two dbd.SiH groups per
15 molecule by intimately contacting such fusible polycarbo-
16 silane with an effective hardening amount of the vapors of
17 sulfur and then pyrolyzing the infusible polycarbosilane
18 which results under an ammonia atmosphere.

1 U. S. Patent No. 4,847,027 teaches a method for the
2 preparation of ceramic materials or articles by the pyrolysis
3 of pre-ceramic polymers wherein the pre-ceramic polymers are
4 rendered infusible prior to pyrolysis by exposure to gaseous
5 nitric oxide. Ceramic materials with low oxygen content,
6 excellent physical properties, and good thermal stability can
7 be obtained by the practice of this process. This method is
8 especially suited for the preparation of ceramic fibers.

9 U.S. Patent No. 5,714,025 teaches a method for preparing
10 a ceramic-forming pre-preg tape which includes the steps of
11 dispersing in water a ceramic-forming powder and a fiber,
12 flocculating the dispersion by adding a cationic wet strength
13 resin and an anionic polymer, dewatering the flocculated
14 dispersion to form a sheet, wet pressing and drying the sheet,
15 and coating or impregnating the sheet with an adhesive
16 selected from the group consisting of a polymeric ceramic
17 precursor, and a dispersion of an organic binder and the
18 materials used to form the sheet. The tape can be used to

1 form laminates, which are fired to consolidate the tapes to a
2 ceramic.

3 U. S. Patent No.5,707,471 teaches a method for preparing
4 fiber reinforced ceramic matrix composites which includes the
5 steps of coating refractory fibers, forming the coated fibers
6 into the desired curing the coated fibers to form a pre-preg,
7 heating the pre-preg to form a composite and heating the
8 composite in an oxidizing shape, environment to form an in
9 situ sealant oxide coating on the composite. The refractory
10 fibers have a interfacial coating thereon with a curable pre-
11 ceramic polymer which has a char containing greater than about
12 50% sealant oxide atoms. The resultant composites have good
13 oxidation resistance at high temperature as well as good
14 strength and toughness.

15 U. S. Patent No. 5,512,351 teaches a new pre-preg
16 material which has good tack drape properties and feasible
17 out-time. The pre-preg material is prepared by impregnating
18 inorganic fibers with a composition which includes a fine

1 powder of a metal oxide or oxides having an average particle
2 diameter of not larger than one micrometer, a soluble
3 siloxane polymer having double chain structure, a
4 trifunctional silane compound having at least one
5 ethylenically unsaturated double bond in the molecule
6 thereof, a organic peroxide and a radically polymerizable
7 monomer having at least two ethylenically unsaturated double
8 bonds and heating the impregnated fibers.

9 U. S. Patent No. 4,835,238 teaches a reaction of 1,1-
10 dichloro-silacyclobutanes with nitrogen-containing
11 difunctional nucleophiles which gives polysilacyclobuta-
12 silazanes which can be crosslinked and also converted to
13 ceramic materials.

14 Numerous processing mechanics with various direct
15 applications have been described, for example, in the U. S.
16 Patent No. 5,820,483, U. S. Patent No. 5,626,707, U. S.
17 Patent No. 5,732,743 and U. S. Patent No. 5,698,055. The
18 process mechanics are for a single product process and do

1 not permit continuous curing and pyrolysis in a single step
2 to produce highly dense thick ceramic components.

3 U. S. Patent No. 5,820,483 teaches methods for
4 manufacturing a shaft for a golf club. A plug is detachably
5 affixed to a distal end of a mandrel. A plurality of plies
6 of pre-preg composite sheet are wrapped around the mandrel
7 and plug and, thereafter, heated causing the resin
8 comprising the various plies to be cured. The mandrel is
9 then removed from the formed shaft, leaving the plug as an
10 integral part of the distal tip of the shaft.

11 U. S. Patent No. 5,626,707 teaches an apparatus which
12 produces a composite tubular article. The apparatus includes
13 a frame, a drive mechanism for rotating a mandrel, at least
14 two spindles mounted to the frame, a tensioner and a belt
15 extending between the first and second spindles. The
16 apparatus may be used to roll pre-preg strips or similar
17 sheets of composite materials around the mandrel. The belt
18 travels over the spindles, and the spindles guide the belt

1 through changes in its direction of travel. The mandrel is
2 mounted in the drive mechanism in contact with the belt, which
3 changes its direction of travel around the mandrel. The lower
4 surface of the belt bears against upper portions of the
5 spindles, and the mandrel contacts the upper surface of the
6 belt. As the drive mechanism rotates the mandrel, pre-preg
7 sheets are fed between the mandrel and the belt and are
8 thereby wrapped around the mandrel. The belt presses the pre-
9 preg sheets against the mandrel. The wrapped mandrel may then
10 be removed from the apparatus and cured in any suitable manner
11 known in the art to produce the a composite tubular article.

12 U. S. Patent No. 5,732,743 teaches a method for joining
13 and repairing pipes includes the step of utilizing photo-
14 curable resins in the form of a fabric patch to for quickly
15 repairing or sealing pipes. A photo-curable flexible pre-preg
16 fabric is wrapped over the entire area of the pipe to be
17 joined or repaired. The pre-preg fabric contains multiple
18 layers of varying widths and lengths. The pre-preg fabric is

1 then exposed to photo-radiation which cures and seals the
2 pipe.

3 U. S. Patent No. 5,698,055 teaches a method for making a
4 reinforced tubular laminate. A dry braided fiber sleeve is
5 placed between a mandrel and spiral tape wrap either over,
6 under, or layered with a pre-preg material. During the
7 initial stages of the curing process, while the temperature is
8 rising, the resin in the pre-preg material flows and wets out
9 the dry braid. When the final cure takes place, the braid
10 becomes an integral part of the finished laminate. The choice
11 of fiber materials and braid angle permits various tubular
12 laminate strengths. The selection of fiber colors and
13 patterns permit a wide variety of tubular laminate aesthetic
14 characteristics.

15 U. S. Patent No. 5,632,834 teaches sandwich structures
16 which are made of fiber-reinforced ceramics. The base
17 substance of the ceramic matrix consists of a Si-organic
18 polymer and a ceramic or metallic powder. A cross-linking of

1 the Si-organic polymer takes place under increased pressure
2 and at an increased temperature. After the joining of the
3 facings and the honeycomb core, the sandwich structure is
4 pyrolysed to form a ceramic material

5 U. S. Patent No. 5,641,817 teaches organometallic ceramic
6 precursor binders which are used to fabricate shaped bodies by
7 different techniques. Exemplary shape making techniques which
8 utilize hardenable, liquid, organometallic, ceramic precursor
9 binders include the fabrication of negatives of parts to be
10 made (e.g., sand molds and sand cores for metalcasting, etc.),
11 as well as utilizing ceramic precursor binders to make shapes
12 directly (e.g., brake shoes, brake pads, clutch parts,
13 grinding wheels, polymer concrete, refractory patches and
14 liners, etc.). A thermosettable, liquid ceramic precursors
15 provides suitable-strength sand molds and sand cores at very
16 low binder levels and, upon exposure to molten metal casting
17 exhibit low emissions toxicity as a result of their high char
18 yields of ceramic upon exposure to heat. The process involves

1 the fabrication of preforms used in the formation of composite
2 articles. Production costs, and relatively poor physical
3 properties prohibits their inherently large cost of
4 capitalization, high wide use.

5 U. S. Patent No. 4,631,179 teaches this ring-opening-
6 polymerization reactions method to obtain a linear polymer
7 of the formula $[\text{SiH}_{.2} \text{CH}_{.2}]_{.n}$. This polymer
8 exhibit ceramics yields up to 85% on pyrolysis. The
9 starting material for the ring-opening-polymerization
10 reaction was the cyclic compound $[\text{SiH}_{.2} \text{CH}_{.2}]_{.2}$
11 which is difficult and costly to obtain in pure
12 form by either of the procedures that have been reported.

13 U. S. Patent No. 5,888,641 teaches an exhaust manifold
14 for an engine which are made of all fiber reinforced ceramic
15 matrix composite material so as to be light weight and high
16 temperature resistant. A method of making the exhaust
17 manifold includes the steps of forming a liner of a cast
18 monolithic ceramic material containing pores, filling the

1 pores of the cast monolithic ceramic material with a pre-
2 ceramic polymer resin, coating reinforcing fibers with an
3 interface material to prevent a pre-ceramic polymer resin
4 from adhering strongly to the reinforcing fibers, forming a
5 mixture of a pre-ceramic polymer resin and reinforcing
6 fibers coated with the interface material, forming an
7 exhaust manifold shaped structure from the mixture of the
8 pre-ceramic polymer resin and the reinforcing fibers coated
9 with the interface material by placing the mixture on at
10 least a portion of the cast monolithic ceramic material,
11 and firing the exhaust component shaped structure at a
12 temperature and a time sufficient to convert the pre-ceramic
13 polymer resin to a ceramic thereby forming a reinforced
14 ceramic composite.

15 U. S. Patent No. 5,153,295 teaches compositions of
16 matter which have potential utility as precursors to silicon
17 carbide. These compositions are obtained by a Grignard
18 coupling process starting from chlorocarbosilanes, a readily

1 available class of compounds. The new precursors
 2 constitute a fundamentally new type of polycarbosilane that
 3 is characterized by a branched, $[\text{Si}-\text{C}]_{\text{sub.n}}$ "backbone"
 4 which consists of $\text{SiR}_{\text{sub.3}} \text{CH}_{\text{sub.2}}--$, $--\text{SiR}_{\text{sub.2}}$
 5 $\text{CH}_{\text{sub.2}}--$, $\text{.dbd.SiRCH}_{\text{sub.2}}--$, and $\text{.tbd.SiCH}_{\text{sub.2}}--$
 6 units (where R is usually H but can also be other organic
 7 or inorganic groups, e.g., lower alkyl or alkenyl, as may be
 8 needed to promote crosslinking or to modify the physical
 9 properties of the polymer or the composition of the final
 10 ceramic product). A key feature of these polymers is that
 11 substantially all of the linkages between the Si-C units
 12 are "head-to-tail", i.e., they are Si to C. The
 13 polycarbosilane " $\text{SiH}_{\text{sub.2}} \text{CH}_{\text{sub.2}}$ " has a carbon to
 14 silicon ratio of 1 to 1 and where substantially all of the
 15 substituents on the polymer backbone are hydrogen. This
 16 polymer consists largely of a combination of the four
 17 polymer "units": $\text{SiH}_{\text{sub.3}} \text{CH}_{\text{sub.2}}--$, $--\text{SiH}_{\text{sub.2}} \text{CH}_{\text{sub.2}}$
 18 $--$, $\text{.dbd.SiHCH}_{\text{sub.2}}--$, and $\text{.tbd.SiCH}_{\text{sub.2}}--$ which are

1 connected "head-to-tail" in such a manner that a complex,
2 branched structure results. The branched sites introduced
3 by the last two "units" are offset by a corresponding number
4 of $\text{SiH}_{.3} \text{CH}_{.2}$ -- "end groups" while maintaining the
5 alternating Si--C "backbone". The relative numbers of the
6 polymer "units" are such that the "average" formula is
7 $\text{SiH}_{.2} \text{CH}_{.2}$. These polymers have the advantage that
8 it is only necessary to lose hydrogen during pyrolysis, thus
9 ceramic yields of over 90% are possible, in principle. The
10 extensive Si--H functionality allows facile crosslinking and
11 the 1 to 1 carbon to silicon ratio and avoids the
12 incorporation of excess carbon in the SiC products that are
13 ultimately formed. The synthetic procedure employed to make
14 them allows facile modification of the polymer, such as by
15 introduction of small amounts of pendant vinyl groups, prior
16 to reduction. The resulting vinyl-substituted " $\text{SiH}_{.2}$
17 $\text{CH}_{.2}$ " polymer has been found to have improved
18 crosslinking properties and higher ceramic yield.

1 A pre-ceramic polymer is prepared by a thermally
2 induced methylene insertion reaction of polydimethylsilane.
3 The resulting polymer is only approximately represented by
4 the formula $[\text{SiHMeCH}_2]_n$, as significant amounts
5 of unreacted $(\text{SiMe}_2)_n$ units, complex rearrange-
6 ments, and branching are observed. Neither the preparation
7 nor the resulting structure of this precursor are therefore
8 similar to the instant process. In addition to the
9 carbosilane "units", large amounts of Si--Si bonding remains
10 in the "backbone" of the polymer. This polymer, in contrast
11 to the instant process, contains twice the stoichiometric
12 amount of carbon for SiC formation. The excess carbon must
13 be eliminated through pyrolytic processes that are by no
14 means quantitative. Despite the shortcomings, this polymer
15 has been employed to prepare "SiC" fiber. However, it must
16 be treated with various crosslinking agents prior to
17 pyrolysis which introduce contaminants. This results in a
18 final ceramic product that contains significant amounts of

1 excess carbon and silica which greatly degrade the high
2 temperature performance of the fiber.

3 SiC precursors predominately linear polycarbo-silanes
4 have been prepared via potassium dechlorination of chloro-
5 chloromethyl-dimethylsilane. The resulting polymers have
6 not been fully characterized, but probably contain
7 significant numbers of Si--Si and CH₂--CH₂ groups
8 in the polymer backbone. The alkali metal dechlorination
9 process used in the synthesis of such materials does not
10 exhibit the selective head-tail coupling found with Grignard
11 coupling. The pendant methyl groups in such materials also
12 lead to the incorporation of excess carbon into the system.

13 In several polymer systems mixtures containing vinylchloro-
14 silanes (such as CH₂.dbd.CH--Si(Me)Cl₂) and
15 Me₂SiCl₂ are coupled by dechlorination with
16 potassium in tetrahydro-furan. U. S. Patent No. 4,414,403
17 and U. S. Patent No. 4,472,591 both teach this method. The
18 "backbone" of the resulting polymers consists of a

1 combination of Si--Si and Si--CH₂ CH(--Si)₂ units.
2 Later versions of this polymer Me(H)SiCl₂ in addition
3 to the Me₂SiCl₂ and are subjected to a sodium-
4 hydrocarbon dechlorination process which does not attack
5 vinyl groups. The resulting polymer consists of a
6 predominately linear, Si--Si "backbone" bearing pendant
7 methyl groups, with some Si--H and Si--CH=CH₂
8 functionality to allow crosslinking on pyrolysis.

9 None of these precursors derived using vinylchloro-
10 silanes are similar to those of the process in that having
11 predominantly Si--Si bonded "backbones", they are
12 essentially polysilanes, not polycarbosilanes. In addition,
13 the carbon in these polymers is primarily in the form of
14 pendant methyl functionality and is present in considerable
15 excess of the desirable 1 to 1 ratio with silicon. The
16 ceramic products obtained from these polymers are known to
17 contain considerable amounts of excess carbon.

18 Polymeric precursors to SiC have been obtained by

1 redistribution reactions of methyl-chloro-disilane
2 (Me.sub.6-x Cl.sub.x Si.sub.2, x=2-4) mixtures, catalyzed by
3 tetraalkyl-phosphonium halides which U. S. Patent No.
4 4,310,481, U. S. Patent No. 4,310,482 and U. S. Patent No.
5 4,472,591 teach. In a typical preparation, elemental
6 analysis of the polymer was employed to suggest the
7 approximate formula [Si(Me).sub.1.15 (H).sub.0.25].sub.n,
8 with n averaging about 20. The reaction is fundamentally
9 different than that involved in the process and the
10 structures of the polymers are also entirely different,
11 involving what is reported to be a complex arrangement of
12 fused polysilane rings with methyl substitution and a
13 polysilane backbone.

14 The formation of carbosilane polymers with pendent
15 methyl groups as by-products of the "reverse-Grignard"
16 reaction of chloromethyl-dichloro-methylsilane. The chief
17 purpose of this work was the preparation of carbosilane
18 rings and the polymeric byproduct was not characterized in

1 detail nor was its use as a SiC precursor suggested.
2 Studies of this material indicate that it has an
3 unacceptably low ceramic yield on pyrolysis. These polymers
4 are related to those described in the instant process and
5 are obtained by a similar procedure, however, they contain
6 twice the required amount carbon necessary for
7 stoichiometric silicon carbide and their use as SiC
8 precursors was not suggested. Moreover, the starting
9 material, chloromethyl-dichloro-methylsilane, contains only
10 two sites on the Si atom for chain growth and therefore
11 cannot yield a structure which contains SiCH_2 --
12 chain units. On this basis, the structure of the polymer
13 obtained, as well as its physical properties and pyrolysis
14 characteristics, must be significantly different from that
15 of the subject process.

16 U. S. Patent No. 4,631,179 teaches a polymer which is
17 a product of the ring-opening polymerization of $(\text{SiH}_2$
18 $\text{CH}_2)_2$ also has the nominal composition SiH_2

1 CH.sub.2 ". However, the actual structure of this polymer
2 is fundamentally and functionally different from that of the
3 instant process. Instead of a highly branched structure
4 comprised of SiR.sub.3 CH.sub.2 --, --SiR.sub.2 CH.sub.2 --,
5 .dbd.SiRCH.sub.2 --, and .tbd.SiCH.sub.2 -- units, the Smith
6 polymer is reported to be a linear polycarbosilane which
7 presumably has only [SiH.sub.2 CH.sub.2] as the internal
8 chain segments. Such a fundamental structural difference
9 would be expected to lead to quite different physical and
10 chemical properties. The fundamental difference in these
11 two structures has been verified by the preparation of a
12 linear polymer analogous to polymer and the comparison of
13 its infrared and H-NMR spectra.

14 Another important difference between the process of
15 Smith and the instant process is the method used to obtain
16 the product polymer and the nature of the starting
17 materials. The [SiH.sub.2 CH.sub.2].sub.2 monomer used by
18 Smith is difficult and expensive to prepare and not

1 generally available, whereas the chlorocarbosilanes used in
2 the instant process are readily available through commercial
3 sources.

4 U. S. Patent No. 4,923,716 teaches chemical vapor
5 deposition of silicon carbide which uses a "single
6 molecular species" and which provides reactive fragments
7 containing both silicon and carbon atoms in equal number
8 this process. Linear and cyclic structures of up to six
9 units are mentioned. These compounds, which include both
10 silanes and carbosilanes, are specifically chosen to be
11 volatile for chemical vapor deposition use, and are
12 distinctly different from the instant process, where the
13 products are polymers of sufficiently high molecular weight
14 that they cross-link before significant volatilization
15 occurs. Such volatility would be highly undesirable for the
16 applications under consideration for the polymers of the
17 instant process, where excessive loss of the silicon-
18 containing compound by vaporization on heating would be

1 unacceptable.

2 The inventors hereby incorporate the above-referenced
3 patents and articles into this application.

4 SUMMARY OF THE INVENTION

5 The present invention is generally directed to a
6 process of forming a photo-curable pre-ceramic polymer for
7 use in for fabricating ceramic matrix composites.

8 In a first separate aspect of the invention the process
9 includes the steps to silicon carbide ceramic.

10 In a second separate aspect of the invention the
11 process includes the steps of reacting sodium acetylide with
12 organo-chlorosilanes and condensing (polymerizing) the
13 resultant organo-(ethynyl)-chloro silane product of step a
14 with an excess of an alkali metal. The process includes
15 the steps preparing a solution of thermoplastic photo-
16 curable pre-ceramic polymer, passing a fiber, tape or fabric
17 through the solution of thermoplastic photo-curable pre-
18 ceramic polymer, applying the pre-preg to a shaped mandrel,

1 using light energy to induce cross-linking of the photo-
2 curable pre-ceramic polymer after application to the
3 mandrel. The thermoplastic pre-ceramic polymer is cured and
4 pyrolyzing the cured thermoplastic pre-ceramic polymer
5 matrix composite material.

6 In a third separate aspect of the invention a
7 single-step process for fabricating continuous ceramic fiber
8 ceramic matrix composites employs a thermoplastic photo-
9 curable pre-ceramic polymer in which the component is shaped
10 by a variety of standard composite fabrication techniques,
11 such as filament winding, tape winding, and woven cloth
12 winding. The process includes steps of passing ceramic
13 fiber monofilament, tow, mat, or woven cloth through a
14 solution of the thermoplastic photo-curable pre-ceramic
15 polymer, applying ceramic fiber monofilament, tow, mat, or
16 woven cloth to a shaped mandrel, using photo-energy of the
17 ultraviolet, visible or infrared light spectrum to induce
18 cross-linking (curing) of the photo-curable pre-ceramic

1 polymer after application to the mandrel and either
2 partially or completely pyrolyzing the now cured pre-ceramic
3 polymer matrix composite material.

4 Other aspects and many of the attendant advantages will
5 be more readily appreciated as the same becomes better
6 understood by reference to the following detailed
7 description.

8 The features of the present invention which are
9 believed to be novel are set forth with particularity in the
10 appended claims.

11 DESCRIPTION OF DRAWINGS

12 Fig. 1 is schematic drawing of an apparatus for making
13 flat plates of ceramic composites from photo-curable pre-
14 ceramic polymers.

15 Fig. 2 is a photograph of the apparatus for making flat
16 plates of Fig. 1.

17 Fig. 3 is schematic drawing of an apparatus for making
18 cylinders of ceramic composites from photo-curable pre-

1 ceramic polymers.

2 Fig. 4 is a photograph of the apparatus for making
3 cylinders of Fig. 3.

4 DESCRIPTION OF THE PREFERRED EMBODIMENT

5 A continuous single step manufacturing process for
6 fabricates dense low-porosity composites using novel cross-
7 linkable pre-ceramic polymers and simple plastic industry
8 technology adapted to the thermoset capability of the pre-
9 ceramic polymer. The process eliminates the multi-cycle
10 polymer impregnation pyrolysis method. The process is a
11 simple controllable production process for fiber reinforced
12 ceramic matrix composites, which can be easily automated
13 into large manufacturing continuous processes. This process
14 combines high-yield cross-linkable pre-ceramic polymers and
15 a single step automated process mechanism to produce ceramic
16 components on the scale of aircraft fuselages, boat hulls,
17 and large single ceramic sheets for space vehicle skin
18 panels. The process provides chemically modified pre-

1 ceramic polymers which are very fluid at temperatures 60° C-
2 100° C, have high ceramic yields by weight of 75-95%,
3 exhibit high purity and can be crosslinked into a thermoset
4 with ultraviolet radiation. The process achieves by a
5 series of chemical substitutions using commercially
6 available polymers to incorporate ethynyl side groups on the
7 polymers, which then contain unstable carbon triple bonds
8 and cross-link, by hydrosilylation with Si-H groups upon
9 photo-exposure. The process is to use the chemical
10 substitution ethynyl side group chemistry to produce SiC,
11 Si₃N₄, Al₂O₃ and Al₃N₄ and TiC upon pyrolysis after photo-
12 exposure. Conversion of precursor polymers like
13 polycarbosilane and polysilazane to poly(ethynyl)-
14 carbosilane and poly(ethynyl)silazane achieve this
15 objective. The process draws a fiber, tape, fabric, woven
16 cloth onto a mandrel or suitable substrate by first passing
17 it through the chemically modified pre-ceramic polymer. The
18 objective of this process is to saturate the fiber, tape,

1 fabric, woven cloth with the very fluid pre-ceramic polymer
2 and then photo-cure it on the mandrel or substrate as the
3 saturated material is drawn along by motorized winding or
4 pulling mechanisms known to the prior art. The process
5 provides a continuous fabrication process to enable making a
6 dense (total porosity <8%) fiber reinforced ceramic
7 composite in a single step. This objective is achieved by
8 compacting each layer of pre-ceramic polymer saturated
9 material onto the already pyrolyzed layer below permitting
10 excess polymer to impregnate this layer. The back-fill
11 allowed here reduces the final component porosity, increases
12 strength and provides a short path for volatiles to escape
13 mitigating interlayer delamination. This layer by layer
14 buildup is continued until the required component thickness
15 is reached.

16 The novel nature of the photocurable pre-ceramic
17 polymer enables a process, which is unique to porous filters
18 not achievable with conventional pre-ceramic polymers. This

1 process employs the ability to thermoset the pre-ceramic
2 polymer into a rubbery hard solid prior to heating. In this
3 form the pre-ceramic polymer can be heated and subsequently
4 pyrolyzed without flowing into unwanted areas of the filter.
5 Because of the ability of this process to produce high yield
6 beta-SiC in near Si-C stoichiometry a matrix or coating is
7 formed upon sintering that is highly receptive to heating
8 with microwave energy. The microwave susceptible porous
9 filter is ideally suited for trapping particulate from
10 diesel engine exhausts and can be regeneratively used by
11 microwave heating to a temperature above the oxidation
12 threshold of the trapped particulate soot. The pre ceramic
13 polymer can be made to form not only SiC but also other
14 ceramic bodies such as Si_3N_4 , BC, LAS, etc.

15 Referring to Fig. 1 in conjunction with Fig. 2 an
16 apparatus 10 for making flat plates of ceramic composites
17 from photo-curable pre-ceramic polymers includes a frame 11
18 with a process bed, a set of fabric rollers 12, a set of

1 guide rollers 13, a set of drive rollers 14, a drive motor
2 15, a compression roller 16, a process head 17 having a
3 light-emitting lamp, a furnace 18, a covering 19 and a
4 source of inert gas and a control panel 20. The source of
5 inert gas provides an inert atmosphere.

6 Referring to Fig. 3 in conjunction with Fig. 4 an
7 apparatus 110 for making cylinders of ceramic composites
8 from photo-curable pre-ceramic polymers includes a dry
9 nitrogen environmental chamber 111, a fabric roller 112, an
10 applicator 113 of a photo-curable pre-ceramic polymer, a
11 take-up mandrel 114, a pressure loaded compaction roller
12 115, a light-emitting lamp 116 and a consolidation and
13 pyrolysis zone 117. The consolidation and pyrolysis zone
14 117 has a heater 118. The fabric roller dispenses woven
15 ceramic fabric.

16 Commercially available polycarbosilanes and
17 polycarbosiloxane polymers could be rendered photo-curable,
18 by high intensity photo-radiation, through the addition of

1 ethynyl side groups to the polymer. The polymer,
2 poly(ethynyl) carbosilane, is rendered into an infusible
3 thermoset upon photo-radiation. The process is able to
4 similarly elevate ceramic yields to ~85 % by weight.

5 It has been demonstrated that various combinations of
6 di-functional and tri-functional silane precursors can be
7 utilized to enhance cross-linking and elevate ceramic yield.
8 Combinations of dichlorodimethylsilane (di-functional) and
9 trichlorophenylsilane (tri-functional) can be employed.
10 Through the addition of branching, or cross-linking, ceramic
11 yields as high as 77% have been obtained. Further, it is
12 possible to doped these polymers, with boron for example, to
13 control sintering and crystallization behavior.

14 While this process allows the addition of ethynyl side
15 groups to potentially a wide range of available pre-ceramic
16 polymers, there are other methods of directly synthesizing
17 poly(ethynyl)carbosilane, which are outlined below. In both
18 of the following reaction paths, tri-functional organotri-

1 chlorosilanes are utilized, in part or in entirety, to
2 permit the introduction of photo-polymerizable side-groups,
3 such as ethynyl groups derived from the reaction of sodium
4 acetylide with chlorosilane.

5 In the first reaction route, sodium acetylide is
6 reacted with the organotrichlorosilane, such as a methyl- or
7 phenyltrichlorosilane, as shown in step 1. Typically, this
8 is performed in a solvent, such as hexane or methylene
9 chloride. The by-product of this reaction is sodium
10 chloride, which is insoluble and can be easily removed by
11 filtration and/or sedimentation (step 2). The resulting
12 organo(ethynyl)chlorosilane can be reacted directly with
13 sodium which is a Würtz type condensation reaction or mixed
14 with an organodichlorosilane prior to the initiation of
15 polycondensation. Assuming that all "R"s are the same, and
16 "a + b = 1", then the following reaction path can be
17 proposed:

Processing Step	Reaction
1. The addition of ethynyl (acetylide) side groups to tri-functional polysilazane reactant.	$a \{ \text{RSiCl}_3 + g \text{ NaC}\equiv\text{CH} \rightarrow$ $\text{RSiCl}_{(3-g)}\text{C}\equiv\text{CH}_g + g \text{ NaCl} \}$
2. Remove NaCl by filtration.	$- ag \text{ NaCl}$
3. The addition of di-functional chain former (optional).	$+ b \{ \text{R}_2\text{SiCl}_2 \}$
4. Condensation of modified precursor solution to produce poly(ethynyl)silazane pre-ceramic polymer through the addition of	$a (\text{RSiCl}_{(3-g)}\text{C}\equiv\text{CH}_g) + b (\text{R}_2\text{SiCl}_2) + 2[a(3-g) +$ $b] \text{Na} \rightarrow 1/n \{ \text{Si}_{(a+b)}\text{R}_{(a+2b)}\text{C}\equiv\text{CH}_{ag} \}_n + 2[a(3-$ $g) + b] \text{NaCl}$

sodium.	
---------	--

Table 1: New processing route 1: Steps and reaction

chemistries to form poly(ethynyl)carbosilane-- Final Product

$$= 1/n\{\text{SiR}_{(a+2b)}\text{C}\equiv\text{CH}_{ag}\}_n.$$

1 In route 1, the photo-cross-linkable ethynyl group
 2 (acetylide) is added prior to the initiation of Würtz type
 3 condensation reaction. In route 2, a method of adding
 4 ethynyl side-groups post-condensation, thereby avoiding the
 5 exposure of the ethynyl ligand to sodium during the pre-
 6 ceramic polymer synthesis is disclosed. In this process,
 7 tri-functional and/or a mixture of di-functional and tri-
 8 functional chlorosilanes are reacted with a sub-
 9 stoichiometric quantity of metallic sodium, sufficient to
 10 bring about an increase in molecular weight and viscosity of
 11 the now pre-ceramic polymer backbone, but leaving a fraction
 12 of the chlorosilane reaction sites unreacted. The resulting
 13 sodium chloride by-product can be removed by filtration
 14 and/or sedimentation (step 2).

1 Following polymer condensation, with unreacted
 2 chlorosilane sites intact, excess sodium acetylide is added
 3 to react with the aforementioned unreacted sites to produce
 4 poly(ethynyl)carbosilane photo-curable pre-ceramic polymer.
 5 The poly(ethynyl)carbosilane pre-ceramic polymer can be
 6 retrieved by solvent evaporation by the application of heat
 7 and/or in vacuo. Assuming that all "R"s are the same, and
 8 "a + b = 1", the final desired reaction product is expressed
 9 in the reaction path below in Table 2.
 10 Table 2: New processing route 2: Steps, and reaction
 11 chemistries, to form poly(ethynyl)carbosilane.

Processing Step	Reaction
1. Mixture of di-functional and tri-functional chlorosilanes reacted with a sub-	$a(RSiCl_3) + b(R_2SiCl_2) + [y/(3a+2b)]Na \rightarrow$ $(1/n) \{ Si_{(a+b)} R_{(a+2b)} Cl_{[(1-y)/(3a+2b)]} \}_n +$ $[y/(3a+2b)] NaCl$

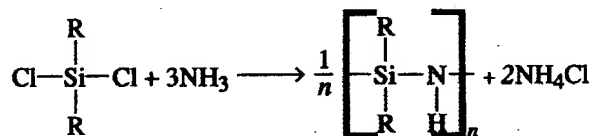
stoichiometric amount of sodium (where $y < [3a+2b]$).	
2. Remove NaCl by filtration and/or sedimentation.	$-[y/(3a+2b)] \text{ NaCl}$
3. Addition of ethynyl side groups to partially condensed polysilazane polymer through the addition of excess sodium acetylide.	$(1/n) \{ \text{Si}_{(a+b)} \text{R}_{(a+2b)} \text{Cl}_{[(1-y)/(3a+2b)]} \}_n$ $+ [(1-y)/(3a+2b)] \text{NaC}\equiv\text{CH} \rightarrow$ $(1/n) \{ \text{Si}_{(a+b)} \text{R}_{(a+2b)} \text{C}\equiv\text{CH}_{[(1-y)/(3a+2b)]} \}_n +$ $[(1-y)/(3a+2b)] \text{NaCl}$

Product = $(1/n) \{ \text{SiR}_{(a+2b)} \text{C}\equiv\text{CH}_{[(1-y)/(3a+2b)]} \}_n$.

- 1 In the previous section, the method of preparing
- 2 poly(ethynyl)carbosilane, a photo-curable pre-ceramic
- 3 polymer precursor to silicon carbide has been reviewed. In
- 4 this section, several of the promising methods of

1 synthesizing polysilazane precursors to silicon nitride
2 (Si_3N_4) and a method of conversion to poly(ethynyl)silazane,
3 a photo-curable pre-ceramic polymer precursor to high yield
4 $\text{Si}_3\text{N}_4/\text{SiC}$ ceramic matrix composites are described. Si_3N_4
5 doped with 10-15 weight percent SiC has significantly lower
6 creep at high temperature than pure Si_3N_4 . The creep rate
7 at the minimum was lower by a factor of three than that of
8 the unreinforced, monolithic matrix of equal grain size.
9 Thus, other researchers have recognized the potential
10 importance of $\text{Si}_3\text{N}_4/\text{SiC}$ nanocomposite matrices for
11 continuous ceramic fiber reinforced composites used in high
12 temperature applications. Two advantages of the process of
13 the process are the ability to fabricate large-scale
14 composites employing existing polymer composite fabrication
15 techniques due to the addition of the photo-cross-linkable
16 ethynyl side-groups and the inclusion of the carbon
17 containing ethynyl group should lead to the addition of
18 approximately 5 to 20 weight percent SiC upon pyrolysis.

1 One of the simplest and direct methods of preparing
 2 polysilazane precursors to silicon nitride, with a 70 weight
 3 percent ceramic yield is to dissolve dichlorosilane in
 4 dichloromethane to yield polysilazane oils. Pyrolysis in
 5 flowing nitrogen gas yielded nearly phase pure α - Si_3N_4 after
 6 heat treatment at 1150°C for 12 hours. Numerous other
 7 permutations and refinements to the preparation of
 8 polysilazane oils and polymers have been developed. The
 9 reaction path of polysilazane formation using
 10 dichlorosilanes and ammonia is set out below:



11 A number of the most direct permutations include
 12 the use of trichlorosilanes, methyltrichlorosilanes,
 13 dimethyldichlorosilanes, and vinyl-, butyl-, phenyl-, ethyl-
 14 , and hexyl- modified chlorosilanes. Increased molecular
 15 weight, and correspondingly increased ceramic yield, can be

1 achieved by catalytically enhancing the cross-linking during
2 final polymer preparation. A number of novel methods,
3 including the use of ruthenium compounds and potassium
4 hydride, have been demonstrated to give ceramic yields upon
5 pyrolysis as high as 85 percent. The inducement of cross-
6 linking prior to pyrolysis is essential to achieving the
7 high ceramic yields necessary to large-scale
8 commercialization of Si_3N_4 matrix composites for high
9 temperature applications. The cross-linking methods cited
10 in the literature, however, are chemical catalysts, making
11 the shaping and forming processes extremely difficult.

12 A ceramic matrix of predominantly silicon nitride with
13 about 10-15 % SiC by weight is nearly ideal for fabricating
14 CMCs. In addition, the catalytic cross-linking of the
15 polysilazane precursor dramatically increases ceramic yield.

16 The synthesis route should produce high yield $\text{Si}_3\text{N}_4/\text{SiC}$
17 nanocomposites employing a photocurable pre-ceramic polymer
18 precursor.

1 One possible method would be to synthesize the
2 unmodified polysilazane through the ammonolysis of various
3 chlorosilane reactants in dichloromethane solvent followed
4 by modifying the resulting polysilazanes, using a previously
5 described process of chlorination followed by attachment of
6 the ethynyl through reaction with sodium acetylide. Another
7 alternative approach starts with a variety of dichloro-
8 silanes and/or trichlorosilanes and reacts them with sodium
9 acetylide at various concentrations, followed by ammonolysis
10 to result in the final poly(ethynyl) silazane precursor as
11 specifically detailed in the Table 3 below:

Processing Step	Reaction
1. addition of acetylide side groups trifunctional polysilazane reactant.	$a \{ \text{RSiCl}_3 + g \text{ NaCCH} \rightarrow \text{RSiCl}_{(3-g)}\text{CCH}_g + g \text{ NaCl} \}$
2. remove NaCl by filtration	$- g \text{ NaCl}$

2. addition of difunctional chain former	$b \{R_2SiCl_2\}$
3. ammonolysis of modified precursor solution to produce poly(ethynyl)silazane pre-ceramic polymer	$a [RSiCl_{(3-g)}CCH_g] + b [R_2SiCl_2] + NH_3$ $\rightarrow b \{[SiR_2(NH)]_n\} + a \{[RSi(NH)_{(3-g)}CCH_g]_m\} + 2[a(3-g) + 2b]NH_4Cl$

Table 3: Processing steps and reaction chemistries to form poly(ethynyl)silazane

1 The following are examples of combining commercially
2 available polymers and catalysts to achieve a final photo-
3 curable pre-ceramic polymer to SiC ceramics. In order to be
4 photo-curable, the polymer requires either double-bonded
5 carbons such as Allyl side groups or triple-bonded carbons
6 such as acetylide or propargyl side groups. The catalysts
7 can include a thermally curable component such as benzoin
8 peroxide and a photo-curable initiator such as Ciba-Geigy's
9 Irgacure 1800™ or a combination of camphorquinone and 2-

1 (dimethylamino)- ethyl methacrylate).

EXAMPLE 1

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Ciba-Geigy's Irgacure 1800	0.02
Photoinitiator 2	None	None

EXAMPLE 2

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Ciba-Geigy's Irgacure 1800	0.02
RT initiator	N,N-dihydroxyparatoluidine	0.02

EXAMPLE 3

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoiniti	Ciba-Geigy's Irgacure 1800	0.01

ator 1		
Photoinitiator 2	none	None

EXAMPLE 4

Category	Compound	Amount (grams)
Polymer	Poly(ethynyl) carbosilane	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Ciba-Geigy's Irgacure 1800	0.02
Photoinitiator 2	none	None

EXAMPLE 5

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Camphorquinone	0.02
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate.	0.02

EXAMPLE 6

Category	Compound	Amount (grams)
Polymer	Poly(ethynyl) carbosilane	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator	Camphorquinone	0.02

ator 1		
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate.	0.02

EXAMPLE 7

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	None
Photoinitiator 1	Camphorquinone	0.02
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate.	0.02

EXAMPLE 8

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Camphorquinone	0.01
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate).	0.01

EXAMPLE 9

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0

Catalyst	Benzoil Peroxide	none
Photoinitiator 1	Camphorquinone	0.01
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate).	0.01

1 All of the above examples cross-linked under photo-
 2 irradiation (using either ultraviolet light or blue light as
 3 indicated) within a few minutes to an hour under continuous
 4 irradiation at room temperature. The samples were
 5 transformed by this method from thermoplastic to thermoset
 6 pre-ceramic polymers which did not flow or deform
 7 significantly upon subsequent heat-treatment and pyrolysis,
 8 ultimately yielding SiC containing ceramics. The examples
 9 are meant to be illustrative. A person trained in the art
 10 can easily modify the ratios and selection of both pre-
 11 ceramic polymer and/or photo-initiators and catalyst
 12 combinations.

13 This process enables the continuous manufacture of
 14 fiber reinforced ceramic composites by the use of high
 15 ceramic yield pre-ceramic polymers which are photo-curable

1 to a thermoset from a thermoplastic state. A composite in
2 any form or shape is fabricated by photocuring each
3 individual layer of fiber with in-situ pyrolysis of the pre-
4 ceramic polymer impregnated into the fiber layer. The layer
5 by layer of fiber, fabric or woven cloth is pressure loaded
6 to press the thermoplastic polymer infiltrated fabric onto
7 the mandrel or flat substrate thereby permitting excess
8 polymer to impregnate the porous, already pyrolyzed, layer
9 below. This single step process allows a shorter mean free
10 path for volatiles to escape with less destruction than the
11 removal of organics from more massive parts, for
12 consolidation of each layer individually, and for increased
13 layer to layer bonding and improved interlaminar shear
14 strengths.

15 Silicon carbide (SiC) is one of several advanced
16 ceramic materials which are currently receiving considerable
17 attention as electronic materials, as potential replacements
18 for metals in engines, and for a variety of other

1 applications where high strength, combined with low density
2 and resistance to oxidation, corrosion and thermal
3 degradation at temperatures in excess of 1000° C are
4 required. Unfortunately, these extremely hard, non-melting
5 ceramics are difficult to process by conventional forming,
6 machining, or spinning applications rendering their use for
7 many of these potential applications problematic. In
8 particular, the production of thin films by solution
9 casting, continuous fiber by solution or melt spinning, a
10 SiC matrix composite by liquid phase infiltration, or a
11 monolithic object using a precursor-based binder/sintering
12 aid, all require a source of SiC which is suitable for
13 solution or melt processing and which possesses certain
14 requisite physical and chemical properties which are
15 generally characteristic of polymeric materials.

16 Polymeric precursors to ceramics such as SiC afford a
17 potential solution to this problem as they would allow the
18 use of conventional processing operations prior to

1 conversion to ceramic. A ceramic precursor should be
2 soluble in organic solvents, moldable or spinnable,
3 crosslinkable, and give pure ceramic product in high yield
4 on pyrolysis. Unfortunately, it is difficult to achieve all
5 these goals simultaneously. Currently available SiC
6 precursor systems are lacking in one or more of these areas.
7 Problems have been encountered in efforts to employ the
8 existing polysilane and polycarbosilane precursors to SiC
9 for preparation of SiC fiber and monolithic ceramic objects.
10 All of these precursors have C/Si ratios considerably
11 greater than one, and undergo a complex series of ill-
12 defined thermal decomposition reactions which generally lead
13 to incorporation of excess carbon. The existence of even
14 small amounts of carbon at the grain boundaries within SiC
15 ceramics has been found to have a detrimental effect on the
16 strength of the ceramic, contributing to the relatively low
17 room-temperature tensile strengths typically observed for
18 precursor-derived SiC fibers.

1 Efforts to develop polymeric precursors to SiC have
2 focused largely on two types of polymers, polysilanes, which
3 have a Si--Si backbone, and polycarbosilanes, in which the
4 polymer backbone is $[-\text{Si}-\text{C}-]_{\text{n}}$. The polysilanes all
5 suffer from problems due to insolubility, infusibility
6 and/or excess carbon incorporation. Certain of the
7 polycarbosilanes have more suitable physical properties for
8 processing; however, in general, these also contain a
9 higher-than-1:1 C:Si ratio and incorporate excess carbon on
10 pyrolysis.

11 In the case of the polycarbosilanes, high molecular
12 weight linear polymers of the type $[\text{R}_{\text{2}}\text{SiCH}_{\text{2}}]_{\text{n}}$, where R is H and/or hydrocarbon groups, have been
13 prepared by ring-opening-polymerization reactions starting
14 from cyclic disilacyclobutanes using chloroplatinic acid and
15 related catalyst systems; however, such linear polycarbo-
16 silanes generally exhibit low yields of ceramic product on
17 pyrolysis due to chain "unzipping" reactions. For example,

1 studies of high molecular weight [Me.sub.2 SiCH.sub.2
2].sub.n polymers have indicated virtually complete
3 volatilization on pyrolysis under an inert atmosphere to
4 1000° C.

5 Use of propargyl groups (HC=CCH₂-), such as propargyl
6 chloride (HC=CCH₂Cl), propargyl bromide (HC=CCH₂Br),
7 propargyl alcohol (HC=CCH₂OH), propargyl magnesium chloride
8 (HC=CCH₂MgCl), propargyl calcium chloride (HC=CCH₂CaCl),
9 propargyl amine (HC=CCH₂NH₂), and other propargyl
10 containing species introduces the photo-curable
11 (Cross-linkable) triple-bonded carbon linkages into the pre-
12 ceramic polymer.

13 U. S. Patent No. 5,153,295 teaches the use of ceramic
14 polymers with an Si-C backbone structure, such as
15 allylhydridopolycarbosilane (AHPCS), formed from the
16 Grignard coupling reaction of a halomethylcarbosilane
17 followed by reduction using a metal hydride in which either
18 a UV cross-linkable ethynyl (i.e. acetylide) or propargyl.

1 group has been introduced into the polymer by methodologies
2 described previously.

3 The use of other ethynyl containing reagents, such as
4 1-ethynyl-1 -cyclohexanol and 1,
5 1'-ethynylenedicyclohexanol, can be directly coupled, due to
6 the presence of hydroxyl (OH) bonds, to either halosilane
7 (Si-X, where X= F, Cl, Br) and/or silanol (Si-OH) groups in
8 the pre-ceramic polymer.

9 The use of benzoyl peroxide or other chemical catalysts
10 in conjunction with double or triple bonded carbon side
11 groups within the pre-ceramic polymer to achieve
12 crosslinking.

13 A single-step fabrication process of continuous ceramic
14 fiber ceramic matrix composites employs a thermoplastic
15 photo-curable pre-ceramic polymer in which the component is
16 shaped by a variety of standard composite fabrication
17 techniques, such as filament winding, tape winding, and
18 woven cloth winding. The process includes steps of

1 passing ceramic fiber monofilament, tow, mat, or woven cloth
2 through a solution of the thermoplastic photo-curable pre-
3 ceramic polymer, applying ceramic fiber monofilament, tow,
4 mat, or woven cloth to a moving flat substrate and using a
5 heated or unheated compaction roller to press the
6 thermoplastic pre-ceramic polymer coated ceramic fiber onto
7 flat substrate. The process also includes the steps of
8 using photo-light of the ultraviolet, visible, or infrared
9 light spectrum to induce cross-linking (curing) of the
10 photo-curable pre-ceramic polymer thereby rendering a
11 thermoset polymer and either partially or completely
12 pyrolyzing the now cured pre-ceramic polymer matrix coated
13 ceramic fiber material. The pre-ceramic polymer
14 poly(ethynyl)carbosilane yields silicon carbide upon
15 pyrolysis. The pre-ceramic polymer may also yield oxide
16 ceramic such as aluminum oxide upon pyrolysis. Other photo-
17 curable pre-ceramic polymers may yield silicon nitride,
18 aluminum nitride and titanium carbide, for example.

1 A first process of forming a photo-curable pre-ceramic
2 polymer, poly(ethynyl)-carbosilane to silicon carbide
3 ceramic includes the steps of reacting sodium acetylide
4 with organo-chlorosilanes and condensing (polymerizing) the
5 resultant organo-(ethynyl)chlorosilane product of step a
6 with an excess of an alkali metal. The organochlorosilane
7 is selected from a group of one or more of the following:
8 dichlorodimethylsilane, trichloro-phenylsilane (tri-
9 functional), and methyltrichlor.

10 A second process of forming a photo-curable pre-ceramic
11 polymer, poly(ethynyl)-carbosilane to silicon carbide
12 ceramic includes the steps of reacting sodium acetylide
13 with organochloro-silanes and condensing (polymerizing) the
14 resultant organo(ethynyl)-chlorosilane product of step a
15 with an excess of an alkali metal sodium.

16 A third process of forming a photo-curable pre-ceramic
17 polymer, poly(ethynyl)-carbosilane, to silicon carbide
18 ceramic includes the steps of reacting sodium acetylide with

1 a mixture of organodichlorosilanes and organo-
2 trichlorosilanes and condensing (polymerizing) the
3 resultant organo(ethynyl)-chlorosilane product of step a
4 with an excess of an alkali metal.

5 A fourth process of forming a photo-curable pre-ceramic
6 polymer, poly(ethynyl)-carbosilane to silicon carbide
7 ceramic includes the steps of reacting a sub-stoichiometric
8 amount of an alkali metal with organochloro-silanes and
9 reacting the partially polymerized polyorganochlorosilane
10 with sodium acetylide. The organochlorosilane is selected
11 from a group consisting of one or more of the following:
12 dichlorodimethylsilane, trichlorophenylsilane (tri-
13 functional) and methyltrichlorosilane.

14 A fifth process of forming a photo-curable pre-ceramic
15 polymer, poly(ethynyl)-carbosilane to silicon carbide
16 ceramic includes the steps of reacting a sub-
17 stoichiometric amount of sodium metal with
18 organochlorosilanes and reacting the partially polymerized

1 polyorganochlorosilane with sodium acetylide.

2 A sixth process of forming a photo-curable pre-ceramic
3 polymer, poly(ethynyl)carbosilane to silicon carbide
4 ceramic includes the steps of reacting a sub-stoichiometric
5 amount of an alkali metal with a mixture of organodichloro-
6 silanes and organotrichlorosilanes and reacting the
7 partially polymerized polyorganochlorosilane with sodium
8 acetylide.

9 A seventh process of forming a photo-curable pre-
10 ceramic polymer, poly(ethynyl)silazane, to silicon nitride
11 ceramic includes the steps of reacting sodium acetylide with
12 organochlorosilanes and condensing (polymerizing) the
13 resultant organo(ethynyl)chlorosilane product of step a with
14 ammonia.

15 An eighth process of forming a photo-curable pre-
16 ceramic polymer, poly(ethynyl)-silazane to silicon nitride
17 ceramic includes the steps of reacting sodium acetylide with
18 organochlorosilanes and condensing (polymerizing) the

1 resultant organo(ethynyl)-chlorosilane product of step a
2 with ammonia.

3 A ninth process of forming a photo-curable pre-ceramic
4 polymer, poly(ethynyl)silazane, to silicon nitride ceramic
5 includes the steps of reacting sodium acetylide with a
6 mixture of organodichlorosilanes and organotrichloro-silanes
7 and condensing (polymerizing) the resultant organo(ethynyl)-
8 chlorosilane product of step a with ammonia. The
9 organochlorosilane is selected from a group consisting of
10 one or more of the following: dichlorodimethylsilane,
11 trichlorophenylsilane (tri-functional) and methyltrichloro-
12 silane.

13 A tenth process of forming a photo-curable pre-ceramic
14 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
15 includes the steps of reacting a sub-stoichiometric amount
16 of ammonia with organochlorosilanes and reacting the
17 partially polymerized polyorganochlorosilazane with sodium
18 acetylide.

1 An eleventh process of forming a photo-curable pre-
2 ceramic polymer, poly(ethynyl)-silazane to silicon nitride
3 ceramic includes the steps of reacting a sub-stoichiometric
4 amount of ammonia with organochlorosilanes and reacting the
5 partially polymerized polyorganochlorosilazane with sodium
6 acetylide.

7 A twelfth process of forming a photo- curable pre-
8 ceramic polymer, poly(ethynyl)-silazane to silicon nitride
9 ceramic includes the steps of reacting a sub-stoichiometric
10 amount of ammonia with with a mixture of organodichloro-
11 silanes and organotrichlorosilanes and reacting the
12 partially polymerized polyorganochlorosilazane with sodium
13 acetylide.

14 A thirteen process for fabricating a ceramic matrix
15 composites includes the steps of preparing a solution of
16 thermoplastic photo-curable pre-ceramic polymer, passing a
17 pre-preg through the solution of thermoplastic photo-curable
18 pre-ceramic polymer, applying the pre-preg to a shaped

1 mandrel, using light energy to induce cross-linking of the
2 photo-curable pre-ceramic polymer after application to the
3 mandrel whereby the thermoplastic pre-ceramic polymer is
4 curved and pyrolyzing the cured thermoplastic pre-ceramic
5 polymer matrix composite material.

6 A process of forming a photo-curable pre-ceramic
7 polymer, poly(ethynyl)-carbosilane to silicon carbide
8 ceramic includes the steps of (a) reacting sodium acetylide
9 with organo-chlorosilanes and (b) condensing (polymerizing)
10 the resultant organo-(ethynyl)chlorosilane product of step a
11 with an excess of an alkali metal. The organochlorosilane
12 is selected from a group of one or more of the following:
13 dichlorodimethylsilane, trichloro-phenylsilane (tri-
14 functional) and methyltrichlorosilane.

15 A process of forming a photo-curable pre-ceramic
16 polymer, poly(ethynyl)-carbosilane to silicon carbide
17 ceramic includes the steps of (a) reacting sodium acetylide
18 with organochloro-silanes and (b) condensing (polymerizing)

1 the resultant organo(ethynyl)-chlorosilane product of step a
2 with an excess of an alkali metal sodium. The rganochloro-
3 silane is selected from a group consisiting of one or more
4 of the following: dichlorodimethylsilane, trichlorophenyl-
5 silane (tri-functional) and methyltrichlorosilane.

6 A process of forming a photo-curable pre-ceramic
7 polymer, poly(ethynyl)-carbosilane, to silicon carbide
8 ceramic includes the steps of (a) reacting sodium acetylide
9 with a mixture of organodichlorosilanes and organotrichloro-
10 silanes and (b) condensing (polymerizing) the resultant
11 organo(ethynyl)-chlorosilane product of step a with an
12 excess of an alkali metal.

13 A process of forming a photo-curable pre-ceramic
14 polymer, poly(ethynyl)-carbosilane to silicon carbide
15 ceramic includes the steps of (a) reacting a sub-
16 stoichiometric amount of an alkali metal with organochloro-
17 silanes and (b) reacting the partially polymerized
18 polyorganochlorosilane with sodium acetylide. The

1 organochlorosilane is selected from a group consisting of
2 one or more of the following: dichlorodimethylsilane,
3 trichlorophenylsilane (tri-functional) and
4 methyltrichlorosilane.

5 A process of forming a photo-curable pre-ceramic
6 polymer, poly(ethynyl)- carbosilane to silicon carbide
7 ceramic includes the steps of (a) reacting a sub-
8 stoichiometric amount of sodium metal with organochloro-
9 silanes and (b) reacting the partially polymerized
10 polyorganochlorosilane with sodium acetylide. The
11 organochlorosilane is selected from a group consisting of
12 one or more of the following: dichlorodimethylsilane,
13 trichlorophenylsilane (tri-functional) and methyltrichloro-
14 silane.

15 A process of forming a photo-curable pre-ceramic
16 polymer, poly(ethynyl)carbosilane to silicon carbide ceramic
17 includes the steps of (a) reacting a sub-stoichiometric
18 amount of an alkali metal with a mixture of organodichloro-

1 silanes and organotrichlorosilanes and (b) reacting the
2 partially polymerized polyorganochlorosilane with sodium
3 acetylide.

4 A process of forming a photo-curable pre-ceramic
5 polymer, poly(ethynyl)silazane, to silicon nitride ceramic
6 includes the steps of (a) reacting sodium acetylide with
7 organochlorosilanes and (b) condensing (polymerizing) the
8 resultant organo(ethynyl)chloro-silane product of step a
9 with ammonia. The organochlorosilane is selected from a
10 group consisting of one or more of the following:
11 dichlorodimethylsilane, trichlorophenylsilane (tri-
12 functional) and methyltrichlorosilane

13 A process of forming a photo-curable pre-ceramic
14 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
15 includes the steps of (a) reacting sodium acetylide with
16 organochlorosilanes and (b) condensing (polymerizing) the
17 resultant organo(ethynyl) chloro-silane product of step a
18 with ammonia. The organochlorosilane is selected from a

1 group consisting of one or more of the following:
2 dichlorodimethylsilane, trichlorophenylsilane (tri-
3 functional) and methyltrichlorosilane

4 A process of forming a photo-curable pre-ceramic
5 polymer, poly(ethynyl)silazane, to silicon nitride ceramic
6 includes the steps of (a) reacting sodium acetylide with a
7 mixture of organodichlorosilanes and organotrichlorosilanes
8 and (b) condensing (polymerizing) the resultant organo-
9 (ethynyl)chloro-silane product of step a with ammonia.

10 A process of forming a photo-curable pre-ceramic
11 polymer, poly(ethynyl)silazane to silicon nitride ceramic
12 includes the steps of (a) reacting a sub-stoichiometric
13 amount of ammonia with organo-chlorosilanes and (b) reacting
14 the partially polymerized polyorganochlorosilazane with
15 sodium acetylide. The organochlorosilane is selected from a
16 group consisting of one or more of the following:
17 dichlorodimethylsilane, trichlorophenylsilane (tri-
18 functional) and methyltrichlorosilane

1 A process of forming a photo-curable pre-ceramic
2 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
3 includes the steps of (a) reacting a sub-stoichiometric
4 amount of ammonia with organochlorosilanes and (b) reacting
5 the partially polymerized polyorganochlorosilazane with
6 sodium acetylide. The organochlorosilane is selected from a
7 group consisting of one or more of the following:
8 dichlorodimethylsilane, trichlorophenylsilane (tri-
9 functional) and methyltrichlorosilane

10 A process of forming a photo-curable pre-ceramic
11 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
12 includes the steps of (a) reacting a sub-stoichiometric
13 amount of ammonia with a mixture of organodichlorosilanes
14 and organotrichlorosilanes and (b) reacting the partially
15 polymerized polyorganochlorosilazane with sodium acetylide.

16 A process for fabricating a ceramic matrix composites
17 includes the steps of (a) preparing a solution of
18 thermoplastic photo-curable pre-ceramic polymer, (b) passing

1 a pre-preg through the solution of thermoplastic photo-
2 curable pre-ceramic polymer, (c) applying the pre-preg to a
3 shaped mandrel, (d) using light energy to induce cross-
4 linking of the photo-curable pre-ceramic polymer after
5 application to the mandrel whereby the thermoplastic pre-
6 ceramic polymer is curved and (e) pyrolyzing the cured
7 thermoplastic pre-ceramic polymer matrix composite material.

8 A first single-step fabrication of continuous ceramic
9 fiber ceramic matrix composites employing a thermoplastic
10 photo-curable pre-ceramic polymer in which the component is
11 shape by a variety of standard composite fabrication
12 techniques, such as filament winding, tape winding, and
13 woven cloth winding includes steps of (a) passing ceramic
14 fiber monofilament, tow, mat, or woven cloth through a
15 solution of the thermoplastic photo-curable pre-ceramic
16 polymer, (b) applying ceramic fiber monofilament, tow, mat,
17 or woven cloth to a shaped mandrel, (c) using photo-energy
18 of the ultraviolet, visible or infrared light spectrum to

1 induce cross-linking (curing) of the photo-curable pre-
2 ceramic polymer after application to the mandrel and (d)
3 either partially or completely pyrolyzing the now cured pre-
4 ceramic polymer matrix composite material. The pre-ceramic
5 polymer is poly(ethynyl)carbosilane. The pre-ceramic
6 polymer may yield silicon carbide upon pyrolysis. The pre-
7 ceramic polymer may yield an oxide ceramic upon pyrolysis.
8 The pre-ceramic polymer may yield titanium carbide upon
9 pyrolysis. The pre-ceramic polymer may yield aluminum
10 nitride upon pyrolysis. The pre-ceramic polymer may yield
11 silicon nitride upon pyrolysis. The pre-ceramic polymer may
12 yield aluminum oxide upon pyrolysis.

13 A second single-step fabrication of continuous ceramic
14 fiber ceramic matrix composites employing a thermoplastic
15 photo-curable pre-ceramic polymer in which the component is
16 shape by a variety of standard composite fabrication
17 techniques, such as filament winding, tape winding, and
18 woven cloth winding under inert atmosphere includes steps of

1 (a) passing ceramic fiber monofilament, tow, mat, or woven
2 cloth through a solution of the thermoplastic photo-curable
3 pre-ceramic polymer, (b) applying ceramic fiber
4 monofilament, tow, mat, or woven cloth to a shaped rotating
5 mandrel, (c) use of a heated or unheated compaction roller
6 to press the thermoplastic pre-ceramic polymer onto the
7 mandrel, (d) using ultraviolet, visible, or infrared light
8 to induce cross-linking (curing) of the photo-curable pre-
9 ceramic polymer thereby rendering a thermoset polymer, (e)
10 either partially or completely pyrolyzing the now cured pre-
11 ceramic polymer matrix material and (f) followed by the
12 final heat treatment of the shaped ceramic matrix composite
13 "brown body". The pre-ceramic polymer is poly(ethynyl)carbo-
14 silane. The pre-ceramic polymer may yield silicon carbide
15 upon pyrolysis. The pre-ceramic polymer may yield an oxide
16 ceramic upon pyrolysis. The pre-ceramic polymer may yield
17 titanium carbide upon pyrolysis. The pre-ceramic polymer
18 may yield aluminum nitride upon pyrolysis. The pre-ceramic

1 polymer may yield silicon nitride upon pyrolysis. The pre-
2 ceramic polymer may yield aluminum oxide upon pyrolysis.

3 A third single-step fabrication of continuous ceramic
4 fiber ceramic matrix composites employing a thermoplastic
5 photo-curable pre-ceramic polymer in which the component is
6 shape by a variety of standard composite fabrication
7 techniques, such as filament winding, tape winding, and
8 woven cloth winding, includes steps of (a) passing ceramic
9 fiber monofilament, tow, mat, or woven cloth through a
10 solution of the thermoplastic photo-curable pre-ceramic
11 polymer, (b) applying ceramic fiber monofilament, tow, mat,
12 or woven cloth to a moving flat substrate, (c) using a
13 compaction roller to press the thermoplastic pre-ceramic
14 polymer coated ceramic fiber onto flat substrate, (d) using
15 photo-light of the ultraviolet, visible, or infrared light
16 spectrum to induce cross-linking (curing) of the
17 photo-curable pre-ceramic polymer thereby rendering a
18 thermoset polymer and (e) either partially or completely

1 pyrolyzing the now cured pre-ceramic polymer matrix coated
2 ceramic fiber material. " The pre-ceramic polymer is
3 poly(ethynyl)carbosilane. The pre-ceramic polymer may yield
4 silicon carbide upon pyrolysis. The pre-ceramic polymer may
5 yield an oxide ceramic upon pyrolysis. The pre-ceramic
6 polymer may yield titanium carbide upon pyrolysis. The pre-
7 ceramic polymer may yield aluminum nitride upon pyrolysis.
8 The pre-ceramic polymer may yield silicon nitride upon
9 pyrolysis. The pre-ceramic polymer may yield aluminum oxide
10 upon pyrolysis.

11 From the foregoing it can be seen that processes of
12 forming a photo-curable pre-ceramic polymer and their
13 applications have been described.

14 Accordingly it is intended that the foregoing
15 disclosure shall be considered only as an illustration of
16 the principle of the present process.